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Investigations at several levels of theory of the quintet states of the CO molecule, which correspond asymptotically to the interaction of $C(^3P)$ + $O(^3P)$, show the $1\,^5\Sigma^+$ state to be a potentially interesting energy storage candidate. Its binding energy (ca. $750\ cm^{-1}$) is sufficiently large compared with those ($<100\ cm^{-1}$) of the other quintets so that one might be able to produce the $1\,^5\Sigma^+$ state preferentially. The decay pathways of the quintets need to be investigated in order to provide a more definitive assessment of their energy storage potential.

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SUMMARY

Investigations at several levels of theory of the quintet states of the CO molecule, which correspond asymptotically to the interaction of $C(^3P) + O(^3P)$, show the $1\,^5\Sigma^+$ state to be a potentially *interesting energy storage candidate. Its binding energy (ca. 750 cm^{-1}) is* sufficiently large compared with those (<100 cm^{-1}) of the other quintets so that one might be able to produce the $1\,^5\Sigma^+$ state preferentially. The decay pathways of the quintets need to be investigated in order to provide a more definitive assessment of their energy storage potential.

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INTRODUCTION

For the purpose of energy storage we seek a molecule such as N_2 or CO which has one or more weakly bound, yet possibly stabilizable, upper states and a very deeply bound ground state. Figure 1 illustrates the concept. It shows, for example, that one might be able to extract about 11 eV for each transition of the weakly bound excited state of CO to the ground state.
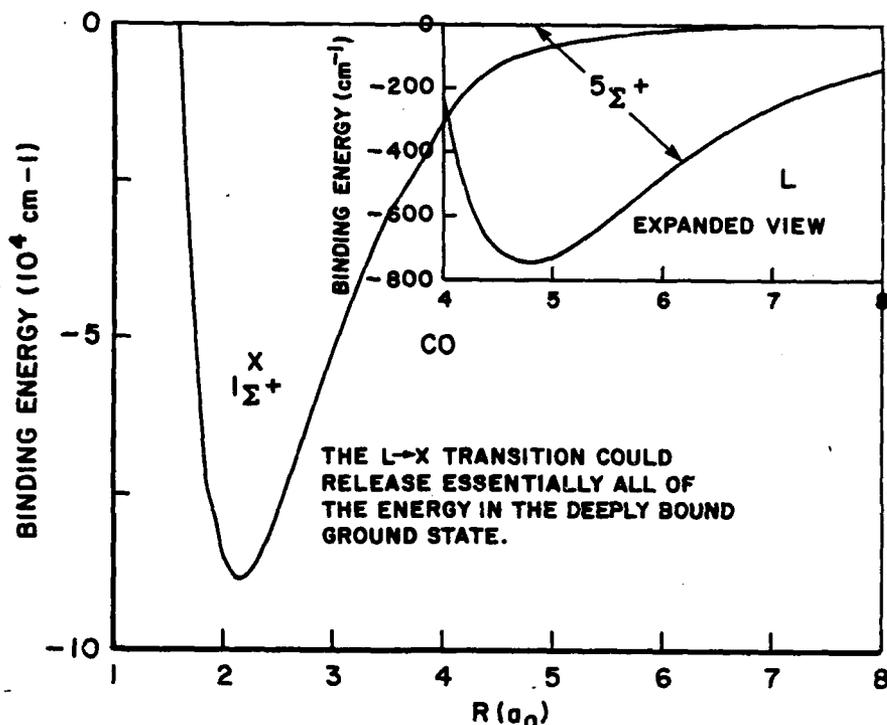
Figure 1. _Potential Energy Release from a High Spin State._

High spin state molecules corresponding to the interaction of ground state atoms are particularly likely candidates for the upper state since they typically will exhibit mainly electrostatic, induction, and dispersion type van der Waals interactions at long-range but no short-range "chemical" binding. Furthermore, such high spin states will have no dipole-allowed transitions to the ground state and thus are potentially long-lived states. Recently, Happer and coworkers (Ref. 1) have argued that $^7\Sigma_u^+$, N_2 (and by implication $^5\Sigma^+$ CO) has spin-spin decay modes that cause it to have an unacceptably short lifetime. Since these decay processes apparently depend on R^{-6} where R is an interfragment distance, molecular size is an important parameter. If we can increase the effective size of the $^5\Sigma^+$ CO by surrounding it with a cluster of H_2 molecules (bound to CO by van der Waals forces), however, we may be able to increase the high-spin lifetime enough so that the cluster

becomes an interesting high energy candidate. Thus, we have launched a detailed study of the quintet states of the CO molecule that has the following main components:

(1)   A preliminary survey of the long-range interactions of ground state C and O atoms by means of a semi-empirical model; .

(2)   Detailed high-quality *ab initio* computations of the potential energy curves for the quintet states of CO which correspond asymptotically to ground state atoms;

(3)   Detailed spin-orbit and spin-spin studies to determine the decay modes of the high-spin CO, and to learn whether the high-spin lifetime can be increased by surrounding CO with a cluster of H_2 or He.

For the sake of clarity and completeness, this report will include portions of the research which had been performed under contract F04611-86-K-0075/P00001 let to the State University of New York. Some of the results of our research have been prepared in form appropriate for publication in <u>Chemical Physics</u>. A semi-final draft of the journal article appears as an appendix to this report. In the first section of this report under "Technical Discussion" I present a summary of the journal article which also serves as a prologue to the *ab initio* investigations.

The next section under "Technical Discussion" comprises a report of our *ab initio* quantum mechanical investigations of the quintet states of CO which correspond to the interaction of ground state carbon and oxygen atoms. This is component (2) mentioned above. First we introduce the problem of the high-spin states of CO and give a review of the very scanty background literature. Then we develop the basis set which is optimized to reproduce relevant energies and electric multipole polarizabilities of the carbon and oxygen atoms. Next we describe the *ab initio* computations of the potential energy curves for the $1,2\ ^5\Sigma^+$, $1\ ^5\Delta$, $1\ ^5\Sigma^-$, and $1,2\ ^5\Pi$ states of CO, and finally we discuss the results. The summary indicates the direction of additional study which is required to estimate the lifetime(s) of these quintet states. That will be component (3), mentioned above, of the study of CO.

TECHNICAL DISCUSSION

The Long-Range Interaction of Ground State Carbon and Oxygen Atoms in the Zero-Overlap Approximation

For our present purposes a reasonable review of the literature of long-range interatomic interactions is given in a few key references (Ref. 2-5). Suffice it to say that the great bulk of the treatments of long-range interactions involve either (a) an empirical approach where the form of the interaction potential is assumed (perhaps guided by theory) and whose parameters are fixed by fitting to experimental data of various kinds, or else (b) a strictly theoretical approach where the energy of interaction is calculated either variationably or using perturbation theory. Typically, the latter approach has been limited to the interaction of ground state species. Recently, Bussery and Aubert-Frecon (Ref. 6-8) have developed a semi-empirical method for estimating the interaction energies of atoms in the "zero-overlap" regime of interatomic separations. Their scheme (which we will call the BAF scheme) overcomes certain limitations of many theoretical approaches, which allows it to be used to describe excited states. The BAF scheme follows the usual perturbation theory development (Ref. 2) to the point where one needs to evaluate the components of the energy expression in the multipole expansion. They recognize that they can use experimental transition moment data and values of experimental atomic energy levels instead of calculated values. When necessary they calculate excited atomic energies by using Whittaker functions to represent the wavefunction. BAF have applied their scheme to various halogen or alkali diatomic molecules with quite notable success as judged by agreement with high quality spectroscopic observations or high quality *ab initio* results.

Bussery and coworkers (Ref. 9) have applied the BAF scheme to the interaction of ground state $C(^3P_J)$ and $O(^3P_J)$ atoms. They find that the long-range interaction energy may be represented by the multipole expression

$$E(R) \approx C_5 R^{-5} + C_6 R^{-6} + C_8 R^{-8} + C_{10} R^{-10} + ... \qquad (1)$$

The $C_5 R^{-5}$ term represents the energy contribution due to the electrostatic interaction of the permanent quadrupole in C with that in O; that term may be either positive, negative, or zero depending on the coupling of the atomic angular momenta to produce a particular molecular state. The remaining terms in Eq. (1) represent the various components of the dispersion interaction energy which corresponds to the interaction of mutually induced multipoles. For example, the term $C_6 R^{-6}$ represents the interaction of an induced dipole on C with an induced dipole on O. The magnitude of C_6 depends on the particular state which results from the interaction of the atoms, but its sign is intrinsically negative (thus, the interaction is always attractive) only so long as both interacting atoms are in their ground electronic states. The higher order terms correspond to the interactions involving higher order induced multipoles.

Bussery and coworkers (Ref. 9) argued that their values of C_5 are relatively reliable but because the experimental values of transition moments and energy levels needed to calculate C_6 in the BAF scheme are so uncertain, they can only obtain crude estimates for C_6. They did not even calculate values of C_8 or C_{10} according to the BAF scheme since the results for the higher coefficients were likely to be even more uncertain. They did find, however, that the C_6 value was roughly the same for all molecular states which correspond to the interaction of ground state C and O atoms.

Since it is clear that only a crude estimate of the zero overlap interaction energy may be obtained presently in any case, we have obtained some rough estimates of the C_6, C_8, and C_{10} coefficients by using the highly approximate expressions 13.3.36 - 13.3.38 of Ref. 1. They are

$$C_6 = (3/2) \, I_C \, I_O \, \alpha_C \alpha_O / (I_C + I_O), \tag{2}$$

$$C_8 = \left(\frac{45}{8e^2}\right)(I_C I_O \alpha_C \alpha_O)\left[\frac{I_C \alpha_C}{2I_C + I_O} + \frac{I_O \alpha_O}{2I_O + I_C}\right], \tag{3}$$

$$C_{10} = \left(\frac{315}{16e^4}\right)(I_C I_O \alpha_C \alpha_O)^2 / (I_C + I_O), \tag{4}$$

where e is the charge of an electron, and where we have substituted in the corresponding expressions given in Ref. 1 the values (a) the first ionization potential of the atoms for the term $h\upsilon$ and (b) the average value of the dipole polarizability calculated in the section of this report for the α terms. We compare in Table 1 the values of the C_n of Eq. (1) given by Bussery and coworkers with those calculated from Eqs. (2-4).

TABLE 1. Long-range Coefficients of Eq. (1) in a.u.

Source	C_5	C_6	C_8	C_{10}
present	11.2	19.7	317	2950
Bussery and coworkers (Ref. 9)	11.2	13.6	352	—

In any case the long-range analysis suggests that all the quintet states of CO with the possible exception of the 2 $^5\Pi$ state will be attractive in the long range. Each attraction will be balanced by the exchange repulsion at some intermediate separation which consequently gives a minimum in each curve. At sufficiently small separations the quintet potential curves will be repulsive. No matter which estimate of the C_n terms one chooses to use, the long-range analysis suggests that the 1 $^5\Sigma^+$ will be by far the most deeply bound of the quintets corresponding to $C(^3P_J) + O(^3P_J)$. The interaction curves will lie in the order 1 $^5\Sigma^+$ << 1 $^5\Delta$ < 2 $^5\Sigma^+$, 1 $^5\Sigma^-$, 1 $^5\Pi$, < 2 $^5\Pi$ at sufficiently large separations. In the next section we examine these predictions by means of more sophisticated theory in order to learn whether any of the quintets is sufficiently deeply bound to be an interesting energy storage candidate.

Ab Initio Computation of the Interaction Energy Curves for the 1,2 $^5\Sigma^+$, 1 $^5\Delta$, 1 $^5\Sigma^+$, and 1,2 $^5\Pi$ States of CO

I have established the motivation for investigating the quintet states of CO, and in the last section I gave a crude analysis to show that, with the likely exception of the 2 $^5\Pi$ state, the quintets of CO are likely to exhibit long-range (or van der Waals) binding and,

thus, are possible energy storage candidates. Unfortunately, there is presently no experimental spectroscopic data with which to compare these crude predictions. Such a situation is not unique to CO. Although fluorescence from excited sodium vapor was described by Wood (Ref. 10) about 80 years ago, and a few of the lower lying transitions in the molecular singlet manifold were mapped out spectroscopically about 50 years ago by Loomis and Kusch (Ref. 11), it was quantum theoretical computations in the last decade or so (Ref. 12) which first gave reliable information on molecular states not readily accessible from the ground $X\ ^1\Sigma_g^+$ state of Na_2. (And Na_2 is a much simpler molecule than CO!) I am aware of only the pioneering quantum mechanical computations of O'Neil and Schaefer [ONS] (Ref. 13) that even discuss the quintet states of CO. Unfortunately, their work extends only to an internuclear separation of $5a_0$, and the Bussery and coworkers estimates (Ref. 9) are valid at separations no smaller than $7\ a_0$. The ONS results, which are obtained from a full configuration interaction treatment based on a minimal basis set, suggest that one or both of the $1\ ^5\Sigma^+$ and $1\ ^5\Pi$ states are somewhat more deeply bound than one might expect on the basis of the crude long-range analysis discussed in the last section. Consequently, it appears that more detailed computations and analysis are in order.

Basis Set Development

Recall that it is our goal to obtain accurate potential energy curves for the quintet states of CO which correspond asymptotically to the interaction of $C(^3P)$ and $O(^3P)$. Since we presume these molecular states to be weakly bound van der Waals states, it is doubly important that the basis sets for these calculations be carefully chosen.

For both atoms we began with the 15 function Slater basis sets of McLean and Liu [ML] (Ref. 14) which are given in Table 2. The starting bases were augmented by a Rydberg 3s and a Rydberg 3p function (so that all the molecular calculations will have orbitals with some Rydberg character). We discuss the optimization procedure later. We further augmented and/or changed the basis to include polarizing functions. The latter are necessary to account for the polarization of an atom's charge distribution when another atom or a molecule is brought near it. These polarization effects are the driving forces behind the formation of van der Waals interactions. In all cases, we re-optimized the most diffuse 3d functions of the original ML bases for the dipole polarizability, we optimized an added 4f function for the quadrupole polarizability, and we optimized an added 5g function for the octupole polarizability. Furthermore, we performed a test for the carbon atom to see if adding a p function improved the quadrupole polarizability. It did not. In a similar test we added a d function to see if the octupole polarizability was changed significantly by its addition. The octupole polarizability of C was changed by about 3% (from 699 a_0^7 to 719 a_0^7) by adding a 3d function. This was not deemed a large enough change to include it in an already very large basis. However, it indicates that the error in the octupole polarizability is relatively small. The additions and changes to the ML basis are given in Table 2.

A few words about the optimization procedure are in order. We used the ALCHEMY (Ref. 15) system's Slater integrals and SCF programs to optimize (i.e., minimize) the energy of Rydberg states of the atoms. For carbon, this was done by minimizing the energy with respect to the added functions of the triplet P states with the following electron configurations: $1s\sigma^2\ 2p\sigma\ 3s\sigma^2\ 2p\pi$ (to obtain the 3s functions) and $1s\sigma^2\ 1s\sigma^2\ 2s\sigma^2\ 2p\sigma\ 3p\pi$ (to obtain the 3p functions). It should be noted that these are not the lowest energy states of carbon containing 3s and 3p orbitals. However, in a single configuration calculation the 2s(2p) orbitals have to be removed to prevent orbital

degeneracies from occurring. For oxygen, we added the 3s and 3p functions and optimized the SCF energy of the quintet S and P states.

TABLE 2(a). Modifications of the McLean and Liu (Ref. 14) 6s, 4p, 3d, 2f Slater Basis Sets for C and O to Add Rydberg Character and Improve Multipole Polarizabilities.

seq #	n	1	ζ values	
			carbon	oxygen
1	1	0	9.4826	13.7574
2	1	0	5.4360	7.6141
3	2	0	4.2010	5.8660
4	2	0	2.6844	4.3120
5	2	0	1.5243	2.4802
6	2	0	1.0575	1.6982
8	2	1	6.5100	7.5648
9	2	1	2.6005	3.4499
10	2	1	1.4436	1.8173
11	2	1	0.9807	1.1439
13	3	2	3.6407	4.8299
14	3	2	2.0211	2.5442
15	3	2	1.3730	1.6015
16	4	3	2.5985	3.2711
17	4	3	1.7653	2.0590

TABLE 2(b). Rydberg and Polarizing Functions. The sequence numbers indicate where these functions belong in the basis set of Table 2(a).

7	3	0	0.60186	0.70536
12	3	1	0.48707	0.54074
15[a]	3	2	0.87500	1.24837
18	4	3	0.92500	1.18750
19	5	4	0.94375	1.16250

[a] This replaces basis function #15 from the original McLean and Liu basis.

To obtain the dipole, quadrupole, and octupole polarizabilities, we used the ATMBIS program of A.C. Wahl as amended by W. J. Stevens (Ref. 16) to include the finite field approximation (Ref. 17). The added (or changed) functions were chosen to maximize the energy difference between the field "on" and the field "off" cases. The maximization process always took place with the function to be added present in either the sigma space (denoted by $M_l = 0$) or else only in the pi orbital space (denoted by $M_l = 1$) (except, of course, for the optimization of the 3s). We determined the final values of the polarizabilities with the optimized functions present in all the appropriate orbital spaces. The polarizabilities and atomic energies we obtained are given in Table 3. There we show that both the sigma ($M_l = 0$) and pi ($M_l = 1$) projections of the polarizabilities and

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TABLE 3. Dipole, Quadrupole and Octupole Polarizabilities of C and O in Atomic Units.

			ML Basis	Present	Meyer and coworkers [a,b]
C	α_d	$M_l = 0$	------	10.102	10.10[a]
	α_d	1	12.362	12.990	13.05[a]
	$\bar{\alpha}_d$		------	12.027	12.07[a]
	γ_d		------	2.888	2.95[a]
	α_q	$M_l = 0$	------	41.60	41.73[b]
	α_q	1	46.49	61.80	61.28[b]
	$\bar{\alpha}_q$		------	55.07	54.76[b]
	γ_q		------	20.20	19.55[b]
	α_o	$M_l = 0$	------	449.57	------
	α_o	1	253.18	697.73	------
	$\bar{\alpha}_o$		------	615.01	------
	γ_o		------	248.16	------
O	α_d	$M_l = 0$	------	5.005	5.14[a]
	α_d	1	4.23	4.540	4.58[a]
	$\bar{\alpha}_d$		------	4.695	4.77[a]
	γ_d		------	−0.465	−0.56[a]
	α_q	$M_l = 0$	------	20.32	20.61[b]
	α_q	1	11.41	14.74	15.05[b]
	$\bar{\alpha}_q$		------	16.60	16.90[b]
	γ_q		------	−5.58	−5.56[b]
	α_o	$M_l = 0$	------	141.542	------
	α_o	1	37.33	98.352	------
	$\bar{\alpha}_o$		------	112.749	------
	γ_o		------	−43.190	------

[a] Ref. 18

[b] Ref. 19

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consequently the average value ($\bar{\alpha}$) and the anistropy (γ) agree nicely with the carefully optimized values of Meyer and coworkers (Ref. 18, 19). The energies we calculated with these basis sets are given in Table 4. There we show that the atomic excitation energy values (ΔE) which we calculate agree reasonably well with experiment (Ref. 20).

TABLE 4. Atomic Energies (in Hartree Atomic Units) and Excitation Energies (in eV) for C and O Atoms.

Atom	State	$-E(SCF)$	$-E(CI)$	ΔE CI Calc	ΔE Expt. (Ref. 20)
C	^3P	37.6886303	37.7800911		
	^1D	0.6315801	0.7316137	1.32	1.26
	^1S	0.5770546	0.6819760	2.67	2.68
O	^3P	74.8102776	74.9767572		
	^1D	0.7299571	0.9032159	2.00	1.97
	^1S	0.6507112	0.8221247	4.21	4.19

Calculation

Either a multi-configuration self consistent field (MCSCF) or a configuration interaction (CI) calculation is needed to obtain relatively reliable potential energy curves for the weakly interacting systems of interest here. At large internuclear separations the molecular orbitals are essentially atomic in nature. Thus, we can represent the electronic structure by the configuration $1s_O^2\ 1s_C^2\ 2s_O^2\ 2s_C^2\ 2p_O^4\ 2p_C^2$, where we have written the atomic orbitals in the ascending order of the approximate energies of the atomic orbitals. Clearly, we must correlate all six of the valence level p electrons, and perhaps also correlate the carbon 2s electrons (for a total of eight). We deemed it to be too expensive to correlate the oxygen 2s electrons as well for a total of ten correlated electrons.

Since the treatment of the 1 $^5\Delta$ and 1 $^5\Sigma^-$ states is quite straightforward, let us discuss those calculations first. We use the output vectors from an SCF calculation for the 1 $^5\Sigma^+$ state as input to the valence MCSCF calculation with six active electrons distributed among two sigma and two pi orbitals. We call this a ($6e^-/2\sigma + 2\pi$) MC computation. The MC computation for the $^5\Sigma^-$ state comprised four configuration state functions (CSF). We used the MC output as the input vectors for a second order CI (SOCI) calculation which comprised all single and double excitations of eight electrons from three σ and two π valence orbitals; we call these a ($8e^-/3\sigma + 2\pi$) CI computation. It comprised 386,389 CSF. We also checked to see how the $8e^-$ CI results were affected by basing them on vectors obtained from an ($8e^-/3\sigma + 2\pi$) MC calculation (which comprised 21 CSF).

The ($8e^-$/$3\sigma + 2\pi$) CI binding energies for the $^5\Sigma^-$ state were insensitive to whether we used the ($6e^-$/$2\sigma + 2\pi$) or the ($8e^-$/$3\sigma + 2\pi$) MC vectors as input. The results listed in Table 5 result from the ($8e^-$/$3\sigma + 2\pi$) SOCI based on ($8e^-$/$3\sigma + 2\pi$) MC vectors. The computations for the $^5\Delta$ state were quite similar to those for the $^5\Sigma^-$ state. The $^5\Delta$ results given in Table 5 correspond to an ($8e^-$/$3\sigma + 2\pi$) SOCI computation comprising 540,163 CSF and which itself is based on an ($8e^-$/$3\sigma + 2\pi$) MC computation comprising 21 CSF. (The SOCI computation step for each point required about 6 h of CPU time on an IBM 3090 computer.).

TABLE 5. The Potential Energies, in Units of $-E_h$, of Low Lying Quintet States of CO Based on a ($8e^-$/$3\sigma + 2\pi$) SOCI.

$R(a_0)$	$1\,^5\Sigma^+$	$2\,^5\Sigma^+$	$^5\Sigma^-$	$^5\Delta$
3.75	112.664062	112.619943		
4.0	112.667000	112.634461	112.631212	
4.1	112.667770	112.640298		
4.25	112.668556	112.646220		
4.5	112.669242	112.653411		
4.75	112.669439	112.658154		
5.0	112.669361	112.661231	112.660436	
5.25	112.669134	112.663194		
5.5	112.668837	112.664421	112.664146	
5.75	112.668517	112.665169		
6.0	112.668202	112.665609	112.665594	112.665850
6.25	112.667908	112.665855	112.665915	
6.5	112.667643	112.665981	112.666094	112.666265
6.75	112.667409	112.666033	112.666184	
7.0	112.667206	112.666042	112.666221	112.666338
7.2	112.667064	112.666033	112.666227	
7.5	112.666884	112.666001	112.666214	112.666297
8.0	112.666653	112.665934	112.666168	112.666228
9.0	112.666375	112.665816	112.666075	
10.0	112.666233	112.665741	112.666015	112.666034
12.0	112.666115	112.665669	112.665959	
20.0	112.666033	112.665616	112.665916	
30.0	112.666025	112.665611	112.665914	112.665912

The computations for the $^5\Sigma^+$ and $^5\Pi$ states were somewhat more involved since there are two states of each symmetry which correspond asymptotically to the interaction of ground state C and O atoms. Let us consider the $^5\Sigma^+$ states. Neither the $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,5\sigma^2\,1\pi^2\,2\pi^2$ configuration which is dominant at large separations for the $1\,^5\Sigma^+$ state nor the $1\sigma^2\,2\sigma^2\,3\sigma^2\,4\sigma^2\,5\sigma\,6\sigma\,1\pi^3\,2\pi$ dominant configuration for $2\,^1\Sigma^+$ correspond asymptotically to ground state carbon and oxygen atoms. However, a proper average of the two molecular configurations does correspond at long-range to ground state atoms.

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Thus, a mix of one part of the $1\ ^5\Sigma^+$ state and two parts of the $2\ ^5\Sigma^+$ state dissociates to ground state atoms. We ran a $(6e^-/2\sigma + 2\pi)$ state averaged MCSCF computation for the $^5\Sigma^+$ states with the weighting $(1/3)\ 1\ ^5\Sigma^+$ and $(2/3)\ 2\ ^5\Sigma^+$. At the internuclear separation $R = 30\ a_0$ we found the two $^5\Sigma^+$ states to be essentially degenerate (the two states were separated by $0.028\ cm^{-1}$) as they should be. A $(6e^-/2\sigma + 2\pi)$ SOCI based on these state averaged (SA) $(6e^-/2\sigma + 2\pi)$ MC output vectors yielded two roots which were separated by $330.29\ cm^{-1}$. Obviously, the energy lowering afforded by excitations to the virtual space is different (by about $330\ cm^{-1}$) for the lowest two $^5\Sigma^+$ states. We then performed a $(8e^-/3\sigma + 2\pi)$ SOCI based on the $(6e^-/2\sigma + 2\pi)$ SAMC vectors and found that the energy separation between the two $^5\Sigma^+$ states was reduced to $90.58\ cm^{-1}$. This SOCI computation comprised 384,539 CSF; the $(6e^-/2\sigma + 2\pi)$ SOCI required 57,898 CSF. A SOCI which correlates ten electrons would presumably decrease the asymptotic non-degeneracy even further. Since such calculations would have required 1,648,672 CSF, we did not carry them out. The results in Table 5 for the $1,2\ ^5\Sigma^+$ states correspond to a $(8e^-/3\sigma + 2\pi)$ SOCI based on $(6e^-/2\sigma + 2\pi)$ SAMC vectors.

The situation for the $1,2\ ^5\Pi$ states is even more complicated. An equal mix of the three configurations $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma\ 1\pi^3\ 2\pi^2$, $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^2\ 6\sigma\ 1\pi^2\ 2\pi$ and $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma\ 6\sigma\ 1\pi^3\ 2\pi$ is needed in order to assure asymptotic dissociation to ground state atoms. Note that the first two configurations are obviously Π configurations while the last one corresponds to the second root of $^5\Sigma^+$ symmetry. The $(6e^-/2\sigma + 2\pi)$ SAMC calculation at $R=30\ a_0$ yields three roots which differ from each other by at most $0.231\ cm^{-1}$. As with the $^5\Sigma^+$ states the splitting between the two $^5\Pi$ states actually became larger when we carried out a SOCI calculation. We found that the $(6e^-/2\sigma + 2\pi)$ SOCI required 108,720 CSF, the $(8e^-/3\sigma + 2\pi)$ SOCI required 705,888 CSF, and the $(10e^-/4\sigma + 2\pi)$ SOCI would have required 3,020,132 CSF had we tried to carry it out. We didn't attempt the latter computation because of the prohibitive expense. In fact, we halted the $^5\Pi$ computations at the $(6e^-/2\sigma + 2\pi)$ SOCI level based on vectors from a 50/50 mixture of $^5\Sigma^+$ and $^5\Pi$ SAMC; these are the results presented in Table 6. Computations at the $(8e^-/3\sigma + 2\pi)$ SOCI based on the proper three-state SAMC are yet to be completed before this work is ready for journal publication.

TABLE 6. The $(6e^-/2\sigma + 2\pi)$ SOCI Potential Energies, in Units of $-E_h$, of the $1,2\ {}^5\Pi$ States of CO Based on a $(6e^-/2\sigma + 2\pi)$ SAMC Which is a 50-50 Mix of ${}^5\Sigma^+$ and ${}^5\Pi$ States.

R	$E(1\,{}^5\Pi)$	$E(2\,{}^5\Pi)$
4.0	112.575931	112.546751
5.0	112.583429	112.578824
5.5	112.584507	112.582940
6.0	112.585499	112.584103
7.0	112.586348	112.584423
8.0	112.586436	112.584449
10.0	112.586391	112.584428
12.0	112.586372	112.584438
20.0	112.586358	112.584443

Discussion of Results and Summary

Because of the problems associated with the asymptotic region, it seems best to discuss the calculated potential energy curves in terms of binding energy curves. We obtained the binding energy curves listed in Table 7 and shown in Figure 2 by taking the zero of energy for each state to be its molecular energy at $R=30\ a_0$. The $(6e^-/2\sigma + 2\pi)$ results we have for the ${}^5\Pi$ states are only preliminary since they are not based on the correct SAMC which assures proper dissociation. Thus, we present in Table 7 only the $1\ {}^5\Pi$ state to indicate its position relative to the Σ and Δ states. The ${}^5\Pi$ states are apparently the most weakly bound of the quintets we consider, while the $1\ {}^5\Sigma^+$ state is the most deeply bound of the quintets we consider. Based on Bussery and coworkers (Ref. 9), one might have expected that the ${}^5\Delta$ state would be slightly more deeply bound than the $2\ {}^5\Sigma^+$ state. However, our results clearly show that $2\ {}^5\Sigma^+$ and $1{}^5\Delta$ and states are nearly degenerate over a wide range of internuclear separations with the $1\ {}^5\Sigma^-$ state slightly less strongly bound. This is rather remarkable qualitative corroboration of the conclusions one can draw from Ref. 9.

Note that the lowest ${}^5\Pi$ state is not at all strongly bound in contrast to the early results of ONS (Ref. 13). While we find the $1\ {}^5\Sigma^+$ state to be the most deeply bound of the quintets we consider, it is not nearly so deeply bound as was suggested by ONS (Ref. 13). We have repeated their CI calculation for the $1\ {}^5\Sigma^+$ state and calculated the basis set superposition error according to the counterpoise scheme of Boys and Bernardi (Ref. 21). We find their superposition error at $R=4.0\ a_0$ to be about 2500 cm^{-1}. This large error is not entirely unexpected since, of necessity, ONS used a minimal basis set in their pioneering work.

TABLE 7. Binding Energies (in cm^{-1}) of the Quintet States of CO Which Correspond Asymptotically to Ground State Carbon and Oxygen Atoms.

R (a$_0$)	1 $^5\Sigma^+$	2 $^5\Sigma^+$	1 $^5\Delta$	1 $^5\Sigma^-$	1 $^5\Pi$
3.75	+430.8	+10023.0			
4.0	-214.0	+6836.6		+7616.0	+8692.7
4.1	-383.0	+5555.6			
4.25	-555.5	+4255.8			
4.5	-706.0	+2677.6			
4.75	-749.3	+1636.6			+642.8
5.0	-732.2	+961.3		+1202.3	
5.25	-682.3	+530.5			
5.5	-617.2	+261.2		+378.8	+406.3
5.75	-546.9	+97.0			
6.0	-477.8	+0.4	+13.6	+70.0	+188.5
6.25	-413.3	-53.6		-0.4	
6.5	-355.1	-81.2	-77.5	-39.7	
6.75	-303.8	-92.6		-59.5	
7.0	-259.2	-94.6	-93.5	-61.6	+2.2
7.2	-228.0	-92.4		-68.9	
7.5	-188.5	-85.6	-84.5	-66.1	
8.0	-137.8	-70.9	-69.4	-56.2	-17.1
9.0	-76.8	-45.0		-35.6	
10.0	-45.7	-28.5	-26.8	-22.4	-7.2
12.0	-19.5	-12.7		-10.1	-6.5
20.0	-1.8	-1.1		-0.7	0.0
30.0	0.0	0.0	0.0	0.0	

It is clear that the 1 $^5\Sigma^+$ state of CO is sufficiently deeply bound to be thermally stable at reasonably low temperatures. Its dissociation energy of ~ 750 cm^{-1} (about 1100 K) is about 4 kT at 0° C and about 14 kT at 77 K. The 1$^5\Sigma^+$ state has over ten bound vibrational energy levels. The 2 $^5\Sigma^+$ and 1 $^5\Delta$ states, which are nearly degenerate, have dissociation energies under 100 cm^{-1} (~ 140 K); the remaining quintets are even more weakly bound.

This suggests a way to populate the 1 $^5\Sigma^+$ state selectively. If a mixture of ground state carbon and oxygen atoms is kept at about 140 K in a magnetic field so that their spins

are kept aligned, all quintets but the $1\,^5\Sigma^+$ state will be thermally unstable. Thus, any atom recombination will form the $1\,^5\Sigma^+$ state preferentially. There may, of course, be less subtle ways to form the CO quintets.
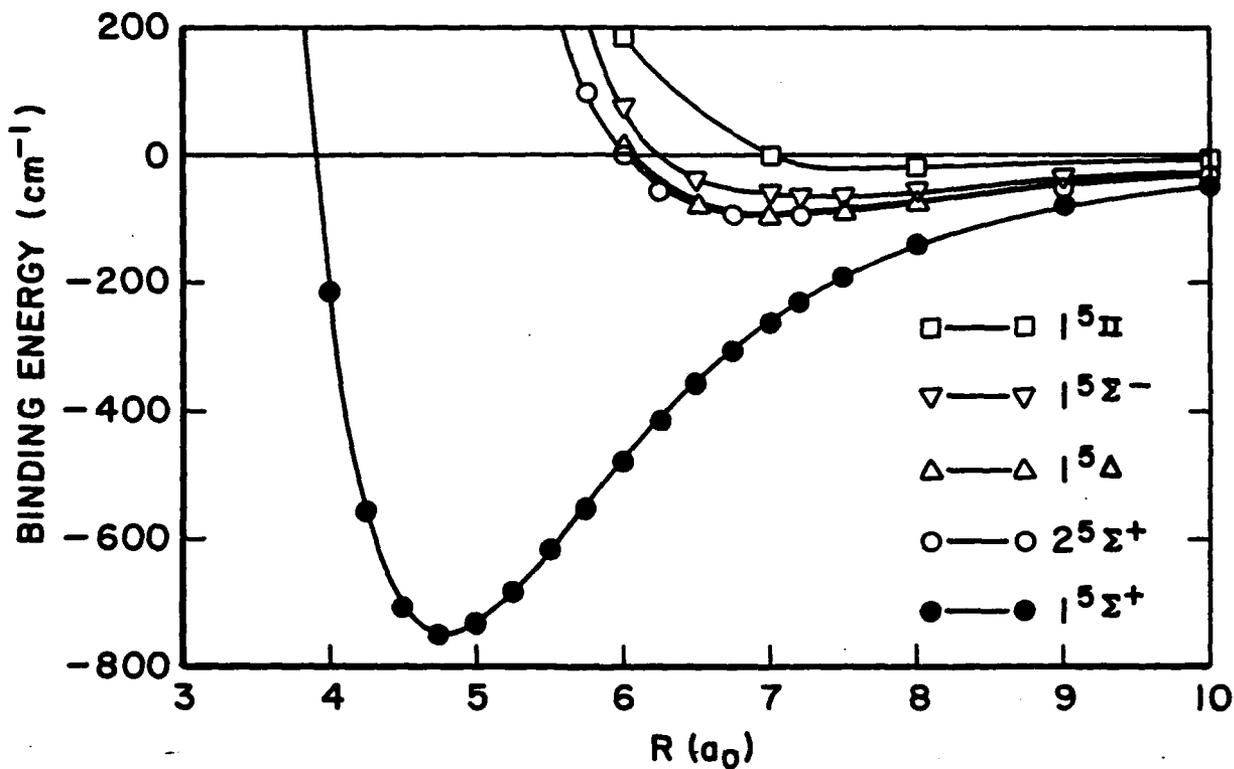

Figure 2. Binding Energy Curves for Quintet States of CO.

Much remains to be learned about the radiative lifetimes of the quintet states and to learn whether there are ways to control the various decay processes, before we can assess fully the potential of high-spin CO as an early storage molecule.

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APPENDIX

Semi-Empirical Determination of the Long-Range Molecular States
Dissociating to $C(^3P_J) + O(^3P_J)$

The following material is an incomplete semi-final draft of a manuscript we have prepared to submit for publication in Chemical Physics. It is intended only to provide the detail necessary to appreciate the contents of the first part of the technical discussion in this report.

SEMI-EMPIRICAL DETERMINATION OF THE LONG-RANGE MOLECULAR STATES DISSOCIATING TO C(^{3}P$_J$) + O(^{3}P$_J$).

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I. Introduction

The theoretical or semi-empirical treatment of the long-range interaction of a pair of atoms is best developed for systems in which the interacting fragments are closed-shell [1] or else where one or both fragments differ from a closed shell electronic configuration by a single electron. For example, the semi-empirical model of Bussery and Aubert-Frecon (BAF) has been quite successful in either predicting or reproducing the very long range interaction energy curves for alkali or halogen diatomic molecules [2-4] as judged by comparison with experimental spectroscopic or exacting theoretical *ab initio* results. The situation is not nearly so sanguine for the interaction of more general open-shell fragments, however. It is our objective in this paper to explore the extension of the BAF model to the interaction of open-shell fragments.

We choose presently to study the interaction of ground-state open-shell C and O atoms. Our motivation for this choice stems in part from the interest in characterizing the weakly bound quintet molecular states resulting in the interaction of atomic C (^3P) + O(^3P) as possible energy storage states. Furthermore, there are new ab initio computations [5] and spectroscopic observations [6] in progress with which to compare our results. Toward this end, we present here the long-range interaction coefficients for the electrostatic and dispersion energies and the resulting potential energy curves which correspond to the C (^3P) + O(^3P) interaction.

In Section II we review the BAF method as applied to the CO molecule. We consider both the [Λ,S] and [J,J] angular momentum coupling schemes which are appropriate, respectively, to the cases where the atomic spin-orbit energy is small or large compared to the interaction energy. We first build up the symmetry-adapted molecules wavefunctions for atoms in their ground term or ground level for these two coupling cases. First order perturbation theory enables us to compute the quadrupole-quadrupole energy terms leading to the C_5 coefficients. Second order perturbation theory gives rise to the induction and dispersion terms characterized by the C_6, C_8,... coefficients.

In Section III we discuss details of the calculations. There we demonstrate the sensitivity of our results to input parameters of the model such as the value of $<r^2>$, the mean square radial position of the electrons in the ground state atoms and the line strengths of electric dipole transitions of the atoms.

In Sections IV and V we examine both Hund's case "a" and case "c" interaction energy curves for internuclear separations $R>2\left[<r_C^2>^{\frac{1}{2}} + <r_O^2>^{\frac{1}{2}} \right]$ suggested by the Le Roy criterion [6]:

(for CO R ~ 6.7 bohr). In the (Λ,S) coupling case the present model suggests somewhat weaker binding than obtained in the *ab initio* computations of Rosenkrantz and coworkers [5]. Due to the strong spin-orbit interaction in oxygen, however, we conclude that the (J,J) coupling scheme must be used for an adequate description of these very long-range interactions.

II. Model

The method we use in this work is basically the same as that already described and used for the halogen and alkali dimers [2-4]. The present summary is consequently brief. We investigate the molecular states due to the interaction of the ground state atoms C and O for internuclear distances sufficiently large so that the overlap between the atomic wavefunctions is presumed to be negligible. Consequently, we neglect overlap and exchange effects. In the usual perturbation theory treatment up to second order we invoke the multipolar expansion of the perturbation operator:

$$V = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \frac{V_{ij}(a,b)}{R^{i+j+1}}$$

where

$$V_{ij}(a,b) = (-)^j \sum_{|m|=0}^{\infty} d_m(i,j) \, Q_m^i(a) \, Q_{-m}^j(b)$$

and

$$d_m(i,j) = (i+j)! \, ((i-m)! \, (i+m)! \, (j-m)! \, (j+m)!)^{-\frac{1}{2}}$$

$$Q_m^i(a) = \sqrt{\frac{4\pi}{2i+1}} \, r_a^i \, Y_i^m(\theta_a, \Phi_a)$$

$(r, \theta, \Phi$ are the spherical polar coordinates).

The spin-orbit separation of 43.4 cm^{-1} for C and 227 cm^{-1} for O validates the LS coupling for the atoms and the Hund's case coupling "c" for the molecule. The molecular states may then be classified following the representation $\Omega^{(\pm)}$ where $\Omega = |M_{Ja} + M_{Jb}|$ is the absolute value of the projection of the total electronic angular momentum along the internuclear axis. The superscripts $\pm$ are related to the states $\Omega = 0$. In this representation the interaction between C(^3P_J) + O(^3P_J) gives rise to 49 molecular states:

states	dissociation
0^+	C($^3P_0$) + O($^3P_0$)
$0^-, 1$	C($^3P_0$) + O($^3P_1$)
$0^-, 1$	C($^3P_1$) + O($^3P_0$)
$0^+, 0^+, 0^-, 1, 1, 2$	C($^3P_1$) + O($^3P_1$)
$0^+, 1, 2$	C($^3P_0$) + O($^3P_2$)
$0^+, 1, 2$	C($^3P_2$) + O($^3P_0$)
$0^+, 0^-, 0^-, 1, 1, 1, 2, 2, 3$	C($^3P_1$) + O($^3P_2$)
$0^+, 0^-, 0^-, 1, 1, 1, 2, 2, 3$	C($^3P_2$) + O($^3P_1$)
$0^+, 0^+, 0^+, 0^-, 0^-, 1, 1, 1, 2, 2, 2, 3, 3, 4$	C($^3P_2$) + O($^3P_2$)

The zero order molecular functions needed in the perturbation procedure are built up as simple products of non-overlapping atomic wavefunctions labeled a and b. Following Chang's [7] procedure each function may be written as:

$$\psi_v = \sum_{k=1}^{n_v} \alpha_{vk} \, |J_k M_k>_a \, |J_k' M_k'>_b$$

The basis functions ψ_v are presented in Appendix I for the 49 molecular states.

We also investigate the interaction between the two ground state atoms C and O where we neglect the spin-orbit effect within each atom. The corresponding molecular states may then be classified following the $^{2S+1}\Lambda^{\pm}$ representation where S is the total spin, Λ is the projection of the total orbital angular momentum on the internuclear axis, the superscripts $\pm$ denoting the symmetry properties of the coordinate wave functions. In this representation (Hund's case coupling "a") the interaction gives rise to 18 molecular states: two states of each symmetry $^{1,3,5}\Sigma^+$, two states of each symmetry $^{1,3,5}\Pi$, one state of each symmetry $^{1,3,5}\Sigma^-$, one state of each symmetry $^{1,3,5}\Delta$, dissociate to $C(^3P) + O(^3P)$. The molecular basis functions derived in Chang's [7] procedure may be written as:

$$\psi_\upsilon = \sum_{k=i}^{n_\upsilon} \alpha_{\upsilon k} \mid S_k \ L_k \ M_{Sk} \ M_{Lk} >_a \mid S'_k \ L'_k \ M'_{Sk} \ M'_{Lk} >_b$$

The expanded forms of the ψ_υ are presented in Appendix II for the 18 molecular states.

The terms in the matrix elements of the interaction energy which depend only on the angular part of the atomic wave functions (quantities A and C in equations (7, 15, 25, 30) of ref [4] remain valid for CO while the terms which depend on the radial part of the atomic wavefunctions take on specific forms. In the particular case of the carbon-oxygen interaction in their ground term ^3P, the initial configuration to be considered is $1s^2 \ 2s^2 \ 2p^2$ for the carbon atom and $1s^2 \ 2s^2 \ 2p^4$ for the oxygen atom. For both of them the optical electron is included in one group of equivalent electrons p^2 or p^4 and has to be decoupled from the others. In the framework of the fractional parentage scheme, the resulting expressions for the various radial quantities are the following:

a)   for the electrostatic energy terms:

$$R_a^i = <(l^n) \ L_a \| Q^i \| (l^n) \ L_a>$$

$$= n \sum_{S_1 L_1} \left[G_{S_1 L_1}^{S_a L_a} \right]^2 (2L + 1)(2l + 1) \tag{1}$$

$$\times \left\{ \begin{array}{ccc} l & L_a & L_1 \\ L_a & l & i \end{array} \right\} \left(\begin{array}{ccc} l & i & l \\ 0 & 0 & 0 \end{array} \right) <nl \mid r^i \mid nl>.$$

R_b^i is given by a relation similar to Eq(1), where primed atomic quantum numbers are used.

The $G_{S_1 L_1}^{SL}$ quantities are the fractional parentage coefficients for the $\{ \mid l^{n-1}[S_1 L_1]l\} l^n SL\}$ configuration [8]. The sum is over the various spectral terms $S_1 L_1$ of the configuration $[l^{n-1}]$. From the selection rules due to the non-zero conditions of the 3j-Wigner coefficients, the only allowed values are $i = i' = 2$ which give rise to a C_5 contribution in the electrostatic energy term:

$$E^{elect} = E_{22}(\upsilon, \lambda) = E_5 (\upsilon, \lambda)/R^5$$

b) for the dispersion energy terms:

$$R^{ii'\,jj'}_{L_a\,L_b} = \sum_{\gamma''_a\,\gamma''_b} \langle\gamma_a\,L_a\,\|\,Q^i\,\|\,\gamma''_a\,L''_a\rangle\langle\gamma''_a\,L''_a\,\|\,Q^{i'}\,\|\,\gamma_a\,L'_a\rangle$$

(2)

$$x\,\langle\gamma_b\,L_b\,\|\,Q_j\,\|\,\gamma''_b\,L''_b\rangle\,\langle\gamma''_b\,L''_b\,\|\,Q^{j'}\,\|\,\gamma_b\,L'_b\rangle\left[\overline{\Delta E}\,(n''_a\,l''_a) + \overline{\Delta E}\,(n''_b\,l''_b)\right]$$

where γ includes all the quantum numbers necessary to represent the electronic state. The sum is carried over all the electronic excited states of each atom. In the particular case of the carbon-oxygen interaction three types of excitation can occur:

i).   Excitation 1^n————1^{n-1} $(n''1'')$

The excited optical electron is one of the (1^n) electron group. Only one group of equivalent electrons needs to be considered. The matrix elements can be written:

$$\langle(1^n)\,L_a\,\|\,Q^i\,\|\,1^{n-1}[S_1L_1]\,n''_a\,l''_a\,L''_a\rangle\langle 1^{n-1}[S_1L_1]\,n''_a\,l''_a\,L''_a\,\|\,Q^{i'}\,\|\,(1^n)\,L_a\rangle$$

$$= n\left[G^{S_aL_a}_{S_1L_1}\right]^2\,(-)^{i+i'+L_a+L''_a}\,(2L_a+1)\,(2L''_a+1)\,(2l+1)\,(2l''_a+1)$$

(2a)

$$\begin{Bmatrix} L_1 & 1 & L_a \\ i & L''_a & l''_a \end{Bmatrix}\begin{Bmatrix} L_1 & l''_a & L''_a \\ i' & L_a & 1 \end{Bmatrix}\begin{pmatrix} 1 & i & l''_a \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l''_a & i' & 1 \\ 0 & 0 & 0 \end{pmatrix}\langle nl\,|\,r^i\,|\,n''_a\,l''_a\rangle\langle n''_a\,l''_a\,|\,r^{i'}\,|\,nl\rangle$$

ii)   Excitation $1^n 1'^p \text{------} 1^{n-1} 1'^{p+1}$

The excitation occurs between two groups of equivalent electrons. The matrix elements are given by:

$$\langle 1^n[S_1L_1] 1'^{p} [S_2L_2] S_aL_a \| Q' \| 1^{n-1} [S_1' L_1'] 1'^{p+1}[S_2' L_2'] S_a'' L_a'' \rangle \langle S_a'' L_a'' \| Q^{i'} \| S_a L_a \rangle$$

$$= n\, 1'^{p+1} \left[G_{S_1'L_1'}^{S_1L_1} \right]^2 \left[G_{S_2'L_2'}^{S_2L_2} \right]^2 (2S_1 + 1)(2S_2' + 1) \left\{ \begin{array}{ccc} S_1' & \frac{1}{2} & S_1 \\ S_2 & S_a'' & S_2' \end{array} \right\}^2 \delta_{S_a S_a''} \sum_{L_3 L_3'} (2L_2' + 1)(-)^{L_a L_a''}$$

(2b)

$$(2L_3 + 1)(2L_3' + 1)(2L_a + 1)(2L_a'' + L)(2l_1 + 1)(2l + L)(2l' + 2) \left\{ \begin{array}{ccc} L_2' & l' & L_3 \\ L_2 & L_a'' & L_2' \end{array} \right\} \left\{ \begin{array}{ccc} L_1' & l' & L_3 \\ L_2 & L_a'' & L_2' \end{array} \right\}$$

$$\left\{ \begin{array}{ccc} L_1 & L_a & L_2 \\ L_a'' & L_3 & i \end{array} \right\} \left\{ \begin{array}{ccc} L_3' & L_a'' & L_2 \\ L_a & L_1 & i' \end{array} \right\} \left\{ \begin{array}{ccc} l & L_2 & L_1' \\ L_3 & l' & i \end{array} \right\} \left\{ \begin{array}{ccc} l' & L_3' & L_1' \\ L_1 & l & i' \end{array} \right\} \left(\begin{array}{ccc} l & i & l' \\ 0 & 0 & 0 \end{array} \right) \left(\begin{array}{ccc} l' & i' & l \\ 0 & 0 & 0 \end{array} \right)$$

$$\langle nl \mid r^i \mid n'l' \rangle \langle n'l'' \mid r^{i'} \mid nl \rangle$$

iii)   Excitation $1^n\, 1^p \text{------} 1^{n-1}\, 1^p\, n''1''$

Two groups of equivalent electrons have to be considered but only one is modified. For that particular case, we give the general expressions for the multipolar transition moments.

$$< (1^n)\, [S_1 L_1]\, 1^{'p}\, [S_2 L_2]\, S_a L_a \parallel Q^i \parallel S_3 L_3\, n''_a\, 1''_a\, L''_a > \tag{2c}$$

$$x\, <S_3 L_3\, n''_a\, 1''_a\, L''_a \parallel Q^{i'} \parallel 1^{n'}\, [S_2 L_1]\, 1^{'p}\, [S_2 L_2]\, S_a L_a>$$

$$= n \left[G^{S_1 L_1}_{S'_1 L'_1} \right]^2 (2S_3 + 1)(2S_1 + 1) \left\{ \begin{array}{ccc} S_3 & \frac{1}{2} & S \\ S_1 & S_2 & S'_1 \end{array} \right\}^2 \delta_{s_a s''_a}(2L_3 + 1)(2L_1 + 1) \left\{ \begin{array}{ccc} L_3 & 1 & L_a \\ L_1 & L_2 & L'_1 \end{array} \right\}^2 (-)^{i+i'+L_a+L''_a}$$

$$x\, (2L_a + 1)(2L''_a + 1) \left\{ \begin{array}{ccc} 1 & L_a & L_3 \\ L'_a & 1''_a & i \end{array} \right\} \left\{ \begin{array}{ccc} 1''_a & L''_a & L_3 \\ L_a & 1 & i' \end{array} \right\} (2l+1)(2l''_a + 1) \left(\begin{array}{ccc} 1 & i & 1''_a \\ 0 & 0 & 0 \end{array} \right) \left(\begin{array}{ccc} 1''_a & i' & 1 \\ 0 & 0 & 0 \end{array} \right)$$

$$x\, <nl \mid r^i \mid n''_a\, 1''_a> <n''_a\, 1''_a \mid r^{i'} \mid nl>$$

For the contribution of atom b, expressions similar to Eqs. 2(a-c) may be derived using the substitutions $L''_a \to L''_b$, $L_a \to L_b$. The selection rules due to the non-zero conditions of the 3j-Wigner coefficients lead to:

$$E^{disp}(\upsilon,\lambda) = \sum_{n=3}^{\infty} E_{2n}(\upsilon, \lambda) / R^{2n}$$

where $2n = i + i'' + j + j''$. Thus, only even powers of R are involved in the multipolar expansion of the dispersion energy.

III. Calculations.

For both the electrostatic and dispersion energy terms whether or not we include spin-orbit effects, we obtain each matrix element as a sum of products of purely angular terms (eqs. 7, 15, 25, 27 of ref. [4]) with radial ones (eq. 5. 1 and 2). Angular terms are computed exactly from the Wigner 3j and 6j coefficients. The numerical evaluation of the radial terms requires the knowledge of the radial wavefunctions for the initial state as well as for all the excited states.

For the investigation of the carbon-oxygen interaction, we have chosen the following approximate wavefunctions:

a)   The Carbon and Oxygen 2p and 2s orbital wave functions displayed in Appendix III have been determined from SCF calculations using the ALCHEMY program [9]. In order to check the quality of the present ground state wave functions, we compare in Table 1 present values with other *ab initio* calculations [10-14] of $<r^2>$. Good agreement is found with Froese-Fischer's Hartree-Fock calculations [12]. But our values are small compared to Desclaux' Dirac-Fock calculation [14] or other recently published data [11] for carbon as well as for oxygen atoms and result in a smaller value of R. To improve the C_5 evaluation, the Desclaux results for $<r^2>$ have been used in our computations.

b)   The excited wavefunctions have been determined in the Coulomb approximation. They are described by a Whittaker function where the effective quantum number υ and the effective charge z^* are determined in the hydrogenic model. That is,

$\upsilon = 1/\left[2(\bar{E}[S_1L_1] - \bar{E}[S_1L_1]\,n1SL)\right]^{\frac{1}{2}}$ and $z^* = n\left[2(\bar{E}[S_1L_1] - \bar{E}[S_1L_1]\,n1SL)\right]^{\frac{1}{2}}$.

Here, $\bar{E}[S_1L_1]n1SL$ is the average value of the experimental electronic state energy defined by:

$$\bar{E}[S_1L_1]n1SL = \sum_J (2J+1)\, E[S_1L_1]n1SLJ \Big/ \sum_J (2J+1)$$

and $\bar{E}[S_1L_1]$ is the average energy value of the $2S_1 + 1L_1$ terms which is equal to or larger than the ionization potential of the neutral atom.

For the n"s series the quantum defect $\rho = n-\upsilon$ is roughly constant, so we represent the excited state by a Whittaker function with an effective quantum number. For the n"d series the effective charge z^* keeps roughly the same value so we represent the excited states by a Whittaker function with an effective charge. For highly excited states not known experimentally, we use a Whittaker function where $\upsilon = n$ and $z^* = 1$ which makes it equivalent to a hydrogenic function. We have limited our evaluation to the determination of the C_6 coefficient for which only the n"s and n"d series are necessary.

In Table 2a and 2b we compare the line strengths for some carbon and oxygen electric dipole transitions computed in this work (using the approximations which we have just described) to other theoretical and experimental values. The line strengths (in a.u.) are related to oscillator strengths or emission transition probabilities by the relations:

$$S = g_i\lambda f_{ik}/303.8 \quad \text{and} \quad S = g_k\lambda^3 A_{ki}/2.0264 \times 10^{18}$$

where g_i and g_k are the statistical weight of the lower and upper state respectively, λ is the transition wavelength in (in Å), f_{ik} is the absorption oscillator strength and A_{ki} is the emission transition probability. Furthermore, we have:

$$S = (2s+1)\,(<\gamma L\,|Q^1|\,\gamma''L''>)^2$$

where s is the atomic spin quantum number and $<\gamma L\,|Q^1|\,\gamma''L''>$ is the dipole transition moment given by Eqs. 2a, 2b and 2c using $i=i'=1$.

Table 2 lists the transition moments we have calculated together with values taken from the literature (15 - 41). We have found few literature values for the $2s^2 2p^2 - 2s\,2p^3 n"1"$ transitions in carbon with which to compare our calculated results. No transition moment or related quantity determination has been reported very recently for that atom. Overall, our approximate values agree best with the experimental results of Boldt [19]. The agreement is good for the [2Po] 3d 3D excitation while our calculated values are small compared to Boldt's for the [2Po] 3s 3P and [2Po] 3d 3P transitions. It should be noted in Table 2-a that there often exist serious discrepancies between the various experimental values of the line strengths, so disagreement with experiment is not necessarily an indication of inadequacies in our calculations.

We have taken for carbon the most recent and presumably most accurate theoretical transition moments given by Froese-Fischer and Saha [38] who used the MCSCF method with Breit-Pauli corrections. A comparison of their transition moment values (listed in the column labeled FF) in Table 2-a with other calculated values shows that correlation effects are apparently quite important for the transition

between $2S^2 2p^2\ ^2P$ and $2S\ 2P^3\ ^3S$, ^3P and ^3D. Nevertheless, discrepancies between theoretical and experimental results still persist and are in some cases important, especially for the $2s.2p^3\ ^3P$ transition. In order to see the influence of this choice, we have also computed the C_6 coefficients using the results of Nicolaides' many body calculations [34] for the $2s\ 2p^3$ transition moments which are seen to be in good agreement with experimental values.

In Table 2-b, we compare our present values for the electric dipole moments for the $2s\ 2p^3\ n"l$ and $2s\ 2p^5$ transitions in oxygen with other theoretical and experimental data. Perhaps the most reliable computed values are those of Froese-Fischer [25] who applied a MCSCF method with Breit-Pauli corrections for the relativistic effects. Our values are too small for the ^3S term while Froese-Fischer's value for the $3s\ ^3S$ term is close to the experimental one. Our present results are close to those due to Armstrong [26] whose extended Coulomb approximation calculations are similar to ours. For the $[^2D^0]\ 3s$ ^3D and $[^2P^0]\ 3s"\ ^3P$ terms, our values are too large while Froese-Fischer's compare well with experiments for the ^3D term. All the theoretical values for the ^3P term are very low compared to the single experimental value. There may be a large error in experimental results for the $[^2P^0]\ 3s"^3P$ transition due to the autoionizing character of that term. Also, Pradhan and Saraph [27] have computed the oscillator strengths for these transitions based on a close coupling method in the frozen-core approximation. Their values are larger than those of Froese-Fischer. For the $n"s"$ and $n"d"$ series, our values are similar to Pradhan and Saraph's [27] and Chung's [28] results for the ^3S and ^3D terms. Chung's calculations are based on the Hartree-Fock single-configuration wavefunctions with a $1s^2\ 2s^2$ frozen core (our core is not frozen). Our values are between those of the two authors for the $n"s"$ series and very close to Chung's values for the $n"d"$ series, but lower than the experimental data [18] for both the $n"s"$ and $n"d"$ series. Our values decrease with $n"$ more quickly than do the experimental ones. This fact may have a non-negligible influence on the C_6 evaluation. A large discrepancy can be seen for the $[^2D^0]3d"\ ^3P$ line strengths between experimental and theoretical determinations. The Froese-Fischer value of the transition probability for the $2s\ 2p^5\ ^3P$ transition in oxygen and is found to lie between experimental and other theoretical results. This value has been included in our computation as well as that of Nicolaides [34] which gives rise to different C_6 values. From these comparisons results the fact that for the first electric dipole transition moments (at least the 3s, 3d excitations), our approximate scheme does not give reliable results. The correlation effects are preponderant in these carbon and oxygen transitions and more complex calculations than the present ones are necessary.

The evaluation of the quantities $R^{ii'}_{jj'}$ requires furthermore the knowledge of all the excited state energies which we take as the experimental ones [35]. We have included 20 excited states in the summation in Eq(2). Higher excited states do not make significant contributions to the long range coefficient value.

IV.   Results and Discussion

We have performed the perturbation theory calculation of the first order quadrupole-quadrupole interactions as well as second order induced dipole-induced dipole interactions for the system $C(^3P_J) + O(^3P_J)$. We write each interaction energy matrix element as:

$$E_{int}(\upsilon,\lambda) = \frac{E_5(\upsilon,\lambda)}{R^5} + \frac{E_6(\upsilon,\lambda)}{R^6} + \delta_{\upsilon\lambda}E_{dis}(\upsilon)$$

where $E_{dis}(\upsilon)$ is the dissociation energy for the molecular state υ. Let us first consider the case where we neglect spin-orbit effects.

Due to the neglect of the exchange contribution the various E_5 and E_6 terms are identical for the multiplets 1, 3, 5 of each symmetry. Thus, the 18 x 18 interaction energy matrix reduces to 4 submatrices. There is one of order 2 for each of symmetries Σ^+ and Π and one of "order 1" for each of the states Δ and Σ^-. (See Appendix IV for explicit expressions of the E_5 and E_6 matrices). For the states Σ^+ and Π, the corresponding submatrices have to be diagonalized for various values of the internuclear separation R, thus providing an interaction energy curve $E_\upsilon(R)$ for each state υ. These curves are shown in Fig. 1.

We have evaluated the energy expressions for values of R starting from 7 a.u. and increasing by steps of 0.1 a.u. The lower limit is suggested by the Le Roy criterion $R > 2\left[<r_C^2> + <r_O^2>\right]^{\frac{1}{2}}$. By a least squares fit of these energy values for each state to the expression:

$$E_\upsilon^*(R) = \frac{C_5(\upsilon)}{R^5} + \frac{C_6(\upsilon)}{R^6} + E_{dis}(\upsilon)$$

allows us to determine fitted values for the two long range coefficients C_5 and C_6 for each molecular state Σ^+ and Π. These values are presented in Table 3.

In the fits we have included increasing values of R until the dissociation limit was reached (at a precision of 0.05 cm^{-1}). Note that under the present assumption of neglecting spin-orbit effects within each atom, the eighteen states correspond to a unique averaged dissociation limit. The values of the C_6 coefficients for the Σ^+, Σ^-, Π and Δ molecular states are all within a factor of two of each other. Thus, the main difference between the various interaction energies results from their different C_5 coefficients.

The different C_6 values which are listed in Table 3 show the sensitivity of these quantities to the choice of the $2s^2 2p^n - 2s 2p^{n+1}$ transition moments and the choice of the first 3s or 3d atomic transition moments. We have computed the C_6 [#1] estimations using the approximations discussed in Section III for all dipole transition moments and Nicolaides' estimates for the $2s^2 2p^n - 2s 2p^{n+1}$ transition moments for carbon ^3S, ^3P, ^3D terms and the oxygen ^3P term [34]. We have computed the C_6 [#2] estimations using these same approximations as in #1 except that here we use Froese-Fischer's estimations for $2s^2 2p^n - 2s 2p^{n+1}$ transition moments in carbon [38] and oxygen [25]. We have computed the C_6 [#3] estimations using values for the first dipole transition moments (3s and 3d excitations) obtained from experiment, correlated computations (selected from Table 2a and 2b) or our own estimates and Froese-Fischer's results for the $2s^2 2p^n - 2s 2p^{n+1}$ transitions moments together with the approximations used in #1 for higher excited states. It is evident that the C_6 coefficients are very sensitive to the determination of the first dipole transition moments which contribute 60% of the total C_6 value (note that this contribution is about 90% for alkali dimers).

A C_6 estimation based on Unsold's approximation has been given by Chang [7]. He estimates C_6 = 20.8 a.u. and C_5 = 10.65 a.u. for the $^{1,3,5}\Sigma^+$ states. Our C_5 value for these molecular states is in good agreement with Chang's determination while our C_6 value is much lower than his estimation. The accuracy of the C_5 depends mainly on the accuracy of the values used for the averaged quantities $<r_C^2>$, $<r_O^2>$ which apparently is good (see Table 1). For the C_6 coefficients, the accuracy of the present determination is limited by the accuracy of the values of the transition moments we use. Note that our

calculated values of these quantities were seen to be in good agreement with (but generally smaller than) those available from experiment or other theoretical calculations. We note also that experimental values, when they are available, are sometimes given with rather large uncertainties. There is a particularly significant spread in the values for the carbon transition 2s $2p^3$ ^3P , for example; different values S = 12.47 [39] or S = 3.62 [34] are at our disposal. The Coulomb approximation gives reasonable transition moments for Carbon and Oxygen excited states as judged by comparison with the available experimental values. Apparently, only the first few transition moments are sensibly affected by correlation effects. Consequently, obtaining improved C_6 values depends sensibly on obtaining more reliable values of the first few transition moments from either theory or experiment. We have found the contribution of the dispersion energy to the long-range interaction energy to be relatively small (C_6 less than 20 a.u.) compared to the quadrupole-quadrupole interaction energy for the 1 Σ^+ and 2 Π states. Indeed, we have at R = 7 a.u. (which is the lower limit of the "pure" long-range interactions) $C_6/(R\ C_5) = 0.11$ for the 1 $^{1,3,5}\Sigma^+$ states and 0.16 for the 2 $^{1,3,5}\Pi$ states. For the $^{1,3,5}\Delta$ states, the dispersion energy due to the induced dipole-induced dipole interaction is of the same order as the electrostatic one. We have $C_6/(C_5*R) = \sim 0.65$. So, for the $^{1,3,5}\Delta$ states, a very accurate C_6 coefficient would be more significant than it is for other states.

No experimental electronic energy curves of the CO molecule are known up to now for internuclear separations as large as 7 a.u. Recently, however, Rosenkrantz, Bohr and Konowalow (RBK) [5] have performed multi-reference second order configuration interaction calculations on the quintet states of CO which correspond asymptotically to the interaction of ground state C and O atoms. With the exception of the 2 $^5\Pi$ state which is essentially repulsive each of the quintets is relatively weakly bound with a potential minimum which lies at an internuclear separation R > 4.75 a_0 (By comparison, the strongly bound ground state has its potential minimum at about 2 a_0). RBK find somewhat greater binding than we do. If we assume that the RBK curves are nearly exact, it is evident that the overlap and exchange effects have a non-negligible contribution to the interaction energy well beyond the limit (6.7 a.u.) given by the Le Roy criterion. The difference between the "pure" van der Waals interactions which we calculate here and the computed energy curves of RBK give us an estimate of exchange and damping effects and the magnitude of the dispersion terms we have neglected for each molecular state. In fact, at such internuclear separations, the interaction energy for all the electronic states dissociating to $C(^3P) + O(^3P)$ (except, possibly, for the Σ^+ states) is small compared with the spin-orbit energy of the oxygen ^3P term. So, the spin-orbit interaction must be taken into account. As a first approximation, we include the spin-orbit energy on each atom and present the electronic energy curves in the so-called Hund's case "c" coupling scheme which gives rise to 49 molecular states.

The 49 x 49 energy matrix E_{int} is factored into 6 submatrices of order 10 for the symmetry 0^+ of order 9 for the symmetry 0^-, of order 15 for the symmetry 1, of order 10 for the symmetry 2, of order 4 for the symmetry 3, and of "order 1" for the state 4. The E_5 and E_6 submatrices are presented in Appendix V (a-e) for the 0^+, 0^-, 1, 2 and 3 symmetries respectively. For the 4 symmetry molecular state, and only for this symmetry, we have $C_5 = E_5$, $C_6 = E_6$ and $C_5(4) = C_5\ (^{1,3,5}\Delta)$, $C_6(4) = C_6\ (^{1,3,5}\Delta)$. For each symmetry we diagonalize the corresponding submatrix for numerous values of R providing $E_\upsilon(R)$ for each state υ. Graphic representation of the 49 molecular states are shown in Fig. 2 (a-e).

Some long-range extrema are seen for the 0^+, 0^-, 1, 2 and 3 symmetry states. We present in Table 4 their position (in a.u.) and interaction energy (in cm^{-1}). The ninth state of symmetry "1" and the eighth state of symmetry "2" have a well depth of 11.8 and 15.5 cm^{-1} respectively. The other states which exhibit a minimum have a well depth less than 5 cm^{-1}; this is smaller than the precision we have on each molecular state and is, consequently, not significant. At shorter internuclear separations the (J,J) coupling

molecular states give rise to the (Λ,S) coupling states. But, as is suggested by the present results shown in Fig. 2, the (Λ,S) coupling scheme is not accurate enough even at $R = 7$ a.u. to represent the long-range interactions of $C(^3P_J) + O(^3P_J)$ except, possibly, for those leading to the Σ^+ states. We give in Fig. 3 a correlation diagram between Hund's case "c" and Hund's case "a" molecular states. By comparing the curves for the various states described by the quantum number Λ or Ω, it appears that the "4" symmetry state comes from the $^5\Delta$ state. We note more particularly that the first "3" symmetry molecular state comes from the $^3\Delta$ state, the second comes from the $^5\Delta$, the third comes from the $1\ ^5\Pi$ state and the fourth comes from the $2\ ^5\Pi$ state.

<h2 style="text-align:center">V.   Summary and Conclusion</h2>

The present paper reports estimations of potential energy curves and long-range coefficients of the molecular states of CO dissociating to $C(^3P_J) + O(^3P_J)$. These interactions give rise to singlet, triplet and quintet Σ^+, Σ^-, Π and Δ molecular states in (Λ,S) coupling or 0^+, 0^-, 1, 2, 3 and 4 symmetry states in (J,J) coupling. They result in a quadrupole-quadrupole interaction (C_5/R^5) energy term due to the permanent quadrupole of each carbon and oxygen atom in their ground state configuration, plus dispersion interactions $(C_6/R^6 + C_8/R^8 + ...)$ energy terms. Since the requisite input data is so uncertain we compute only the induced dipole-induced dipole energy terms (C_6/R^6) for each state. The C_6R^{-6} interactions are quasi independent of the molecular state since C_6 is nearly the same for the Σ^+, Σ^-, Π and Δ states. Furthermore, the C_6/R^6 energy contribution is small relative to the quadrupole-quadrupole energy for the $1\ \Sigma^+$ and $2\ \Pi$ states but is of the same order for the $1\ \Delta$ states while the electrostatic energy vanishes $(C_5 = 0)$ for the $2\ \Sigma^+$, $1\ \Sigma^-$ and $1\ \Pi$ molecular states. The C_5 coefficients are given with a good accuracy while the accuracy of the C_6 coefficients depends mainly on the uncertain quality of the electric dipole moments, especially those evaluated in the Coulomb approximation. The evaluation of the dispersion energy is the most significant shortcoming of the BAF approach as applied to long-range CO interactions. The available data and the approximations which worked so nicely for the alkalies [2-4] are insufficiently accurate for CO. In particular, the atomic electric transition dipole moments (whether obtained from theory or experiment) are highly uncertain. We have noted that even well-correlated computed transition moments [38] may disagree significantly with experimental results. For this molecule, which is probably a "worst case" for the BAF approach, other ways to approximate the dispersion energy may be more reliable. Clearly then, we have not obtained a truly satisfactory description of the dispersion interaction energy. However, in a systematic study of rare gas interactions Krauss and coworkers [1] have found that the neglect of overlap effects leads to an overestimation of the dispersion energy. Thus, our neglecting overlap effects in the induced dipole-induced dipole interaction, which we do treat, compensates, at least in part, for our neglecting the higher order terms.

With the possible exception of the $1\ ^5\Sigma^+$ state, the (Λ,S) coupling case is not accurate enough even at $R = 7$ a.u. due to the strong spin-orbit interaction in the ^3P oxygen atom. So, spin-orbit interactions must be included and the (J,J) coupling case must be considered for an accurate description of the long-range. In that coupling scheme, long-range bound states are predicted for some "1" and "2" symmetry molecular states. Unfortunately, no experimental data to compare these with are known for these long-range molecular states.

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Table 1: Mean-square radii $\langle r^2 \rangle / a_0^2$ of incomplete p shells for carbon and oxygen ^3P term and R/a_0^4 resulting value (a_0 is the Bohr radius)

Ref	Carbon	Oxygen	R
This work	3.74717	1.97801	8.89433
H.F[12]	3.746801	1.974975	8.8798
H.F[12]	3.889709	2.001392	9.3418
H.F.S[13]	3.892540	1.93133	9.0213
D.F[14]	3.88985	2.00067	9.3387
H.F[11]	3.890	2.001	9.341
Ref-7	3.7483	1.9741	8.8794

Table 2a: A comparison of line strengths for some electric dipole transitions in carbon

Transition	Present	F.F.[39]	Other theories	Expt.	$\lambda_{expt}(A)$
$2s2p^3\,^3D^o$	------	5.21	4.71[f], 3.75[e], 3.56[e]	4.2[h], 3.84[a-b], 3.52[c-d]	1561.1
$2s2p^3\,^3P^o$	------	12.47	3.82[f], 3.62[e]	1.5[h], 2.48[d]	1329.3
$2s2p^3\,^3S^o$	------	4.446	7.6[g], 7.62[e]	-----------	945.5
$(^2P^o)3s\,^3P^o$	6.74	------	5.30[f]	8.3[h], 6.52[c]	1657.2
$(^2P^o)4s\,^3P^o$	0.84	------	--------	0.76[h], 1.86[d]	1280.4
$(^2P^o)3d\,^3P^o$	0.65	------	--------	1.1[h], 1.42[i]	1261.3
$(^2P^o)3d\,^3D^o$	2.3	------	--------	2.4[h], 3.406[i]	1277.5

a-D. T. Pegg et al. (1970) [15]
b-M. C. Poulizac et al. (1971) [16]
c-G. M. Lawrence et al. (1966) [17]
d-N. H. Brooks et al. (1977) [18]
e-C. A. Nicolaides et al. (1971-73) [21,34]
f-A. W. Weiss (1967) [22]
g-A. B. Bolotin et al. (1956) [20]
h-G. Boldt (1963) [19]
i-J. Bromander et al. (1978) [40]

Table 2b: A comparison of line strengths for some electric dipole transitions in oxygen

Transition	Present	F.F[25,32]	Other Theories	Expt.	$\lambda_{exp}(A)$
$2s2p^5\ ^3P^o$	----	5.30	4.64[g], 1.63[d], 4.46[k], 2.06[h], 3.45[h]	6.69[f,m]	792.0
$(^4S^o)3s\ ^3S^o$	1.26	1.75	0.91[e], 2.10[d], 1.2[c,j]	1.85[b], 1.81[a,l]	1303.5
4s	0.22	----	0.16[e], 0.29[d]	0.42[a], 0.28[i]	1040.1
5s	0.081	----	0.057[e], 0.097[d]	0.23[a]	977.2
6s	0.040	----	0.0027[e], 0.046[d]	------	951.6
7s	0.022	----	0.015[e]	------	938.5
8s	0.014	----	9.28E-3[e]	------	930.9
9s	9.35E-3	----	6.11E-3[e]	------	926.1
10s	6.57E-3	----	4.24E-3[e]	------	922.9
$(^2D^o)3s\ ^3D^o$	2.4	1.49	1.65[d], 1.6[j,o]	1.7[b], 1.43[a], 1.49[i]	989.5
$(^2P^o)3s\ ^3P^o$	1.62	1.01	2.06[d], 0.96[j,c], 1.92[h], 2.13[h],	3.27[b], 4.01[f]	878.5
$(^4S^o)3d\ ^3D^o$	0.33	----	0.33[e], 0.63[d], 0.31[j]	0.88[a]	1026.6
4d	0.16	----	0.43[d], 0.17[e]	0.34[a]	972.5
5d	0.09	----	0.092[e], 0.18[d]	0.21[a]	949.4
6d	0.053	----	0.054[e], 0.11[d]	0.15[a]	937.3
7d	0.033	----	0.035[e]	0.12[a]	930.2
8d	0.022	----	0.023[e]	------	925.6
9d	0.016	----	0.017[e]	------	922.5
$(^2D^o)3d\ ^3P^o$	0.22	----	0.037[d], 0.18[j], 0.33[h], 0.86[h]	6.41[f]	811.4

a-N. H. Brooks et al. (1977) [18]
b-W. H. Smith et al. (1971)[23]
c-B. H. Armstrong (1966) [26]
d-A. K. Pradhan and H. E. Saraph (1977) [27]
e-S. Chung et al .(1986) [28]
f-E. J. Knystautas et al. (1973) [29]
g-U. I. Safronova (1975) [33]
h-W. L. Luken et al. (1976) [36]
i-C. Zeippen et al. (1977) [37]
j-P. S. Kelly (1964) [24]
k-C. A. Nicolaides (1973) [34]
l-C. A. Nicolaides et al. (1976) [41]
m-G. M. Lawrence (1970) [30]

Table 3: Long-range coefficients C_5 and C_6 for the interactions $C(^3P) + O(^3P)$

Molecular State	Footnote	C_5 (a.u.)	C_6 (a.u.)*
$1\ ^{1,3,5}\Sigma^+$	a	-11.20	-5.81
	b	-11.20	-7.34
	c	-11.20	-8.76
$1\ ^{1,3,5}\Delta$	a	-1.87	-5.16
	b	-1.87	-7.47
	c	-1.87	-8.51
$2\ ^{1,3,5}\Sigma^+$	a	0.	-4.85
	b	0.	-6.42
	c	0.	-7.28
$1\ ^{1,3,5}\Sigma^-$	a	0.	-5.61
	b	0.	-7.92
	c	0.	-9.29
$1\ ^{1,3,5}\Pi$	a	0.	-4.81
	b	0.	-6.08
	c	0.	-6.97
$2\ ^{1,3,5}\Pi$	a	+7.47	-5.70
	b	+7.47	-6.95
	c	+7.47	-8.49

*Extended hydrogenic approximation for all dipole transition moments except:

a. G. A. Nicolaides values [34] for the $2s^2\ 2p^n$ - $2s\ 2p^{n+1}$ transitions.
b. G. Froese-Fischer's values [32,29] for the $2s^2 2p^n$ - $2s\ 2p^{n+1}$ transitions.
c. Correlated calculations, experimental or estimated values for the $2s^2 2p^n$ - $2s^2 2p^{n-1}\ 3s$, 3d transitions and values given by G. Froese-Fischer for the $2s^2\ 2p^n$ - $2s\ 2p^{n+1}$ transitions.

Table 4: Position and Interaction Energy of the long-range extrema of CO dissociating in $C(^3P_J) + O(^3P_J)$

Molecular Symmetry	State no	Extrema Type	Position (a.u.)	Interaction Energy (cm^{-1})
0^+	7	max	~7.	+3.4
	8	min	~8.8	-2.7
		max	~6.8	+1.2
0^-	2	max	~9.7	+1.9
	9	min	~8.2	-2.3
1	7	max	~6.6	+24.9
	9	min	~7.6	-11.8
		max	~7.0	-11.1
	10	max	~6.6	+15.4
	11	min	~7.0	-6.6
		max	~6.4	-3.2
	12	min	~8.6	-1.7
2	5	max	~8.6	+3.1
	6	max	~6.6	+29.8
	8	min	~7.7	-15.5
		max	~6.4	-4.0
	10	min	~8.1	-2.7
3	3	max	~6.5	+33.6

Appendix I: Molecular basis functions for $C(^3P) + O(^3P)$

$E_{diss} + 107.56 \text{ cm}^{-1}$

$$^1\Sigma_0^\pm = \frac{1}{\sqrt{6}}\left\{ |1111\rangle_c|11\text{-}1\text{-}1\rangle_o - |110\text{-}1\rangle_c|110\text{-}1\rangle_o + |11\text{-}11\rangle_c|11\text{-}11\rangle_o \mp|11\text{-}1\text{-}1\rangle_c|1101\rangle_o \mp|110\text{-}1\rangle_c|1101\rangle_o \mp|11\text{-}1\text{-}1\rangle_c|1111\rangle_o \right\}$$

$$^3\Sigma_{+1}^\pm = \frac{1}{2}\left\{ |1111\rangle_c|110\text{-}1\rangle_o - |110\text{-}1\rangle_c|1111\rangle_o \mp|11\text{-}1\text{-}1\rangle_c|1101\rangle_o \pm|1101\rangle_c|11\text{-}1\text{-}1\rangle_o \right\}$$

$$^3\Sigma_0^\pm = \frac{1}{2}\left\{ |1111\rangle_c|11\text{-}1\text{-}1\rangle_o - |11\text{-}1\text{-}1\rangle_c|1111\rangle_o \mp|11\text{-}11\rangle_c|11\text{-}11\rangle_o \right\}$$

$$^3\Sigma_{\text{-}1}^\pm = \frac{1}{2}\left\{ |1101\rangle_c|11\text{-}1\text{-}1\rangle_o - |11\text{-}1\text{-}1\rangle_c|110\text{-}1\rangle_o \mp|110\text{-}1\rangle_c|11\text{-}1\text{-}1\rangle_o \pm|11\text{-}1\text{-}1\rangle_c|1101\rangle_o \right\}$$

$$^5\Sigma_{+2}^\pm = \frac{1}{\sqrt{2}}\left\{ |1111\rangle_c|11\text{-}11\rangle_o \mp|11\text{-}11\rangle_c|1111\rangle_o \right\}$$

$$^5\Sigma_{+1}^\pm = \frac{1}{2}\left\{ |1111\rangle_c|110\text{-}1\rangle_o + |110\text{-}1\rangle_c|1111\rangle_o \mp|11\text{-}11\rangle_c|11\text{-}1\text{-}1\rangle_o \mp|11\text{-}1\text{-}1\rangle_c|11\text{-}11\rangle_o \right\}$$

$$^5\Sigma_0^\pm = \frac{1}{\sqrt{12}}\left\{ |1111\rangle_c|11\text{-}1\text{-}1\rangle_o + 2|1101\rangle_c|110\text{-}1\rangle_o + |11\text{-}1\text{-}1\rangle_c|1111\rangle_o \mp|11\text{-}11\rangle_c|11\text{-}11\rangle_o \pm 2|110\text{-}1\rangle_c|1101\rangle_o \pm|11\text{-}1\text{-}1\rangle_c|1111\rangle_o \right\}$$

$$^5\Sigma_{\text{-}1}^\pm = \frac{1}{2}\left\{ |1101\rangle_c|11\text{-}1\text{-}1\rangle_o + |11\text{-}1\text{-}1\rangle_c|110\text{-}1\rangle_o \mp|110\text{-}1\rangle_c|11\text{-}1\text{-}1\rangle_o \mp|11\text{-}1\text{-}1\rangle_c|1101\rangle_o \right\}$$

$$^5\Sigma_{\text{-}2}^\pm = \frac{1}{\sqrt{2}}\left\{ |11\text{-}11\rangle_c|11\text{-}1\text{-}1\rangle_o \mp|11\text{-}1\text{-}1\rangle_c|11\text{-}11\rangle_o \right\}$$

$$^1\Sigma_1^+ = \frac{1}{\sqrt{3}}\left\{ |1110\rangle_c|11\text{-}10\rangle_o - |1100\rangle_c|1100\rangle_o + |11\text{-}10\rangle_c|1110\rangle_o \right\}$$

$$^3\Sigma_{+1}^+ = \frac{1}{\sqrt{2}}\left\{ |1110\rangle_c|1100\rangle_o - |1100\rangle_c|1110\rangle_o \right\}$$

$$^3\Sigma_0^+ = \frac{1}{\sqrt{2}}\left\{ |1110\rangle_c|11\text{-}10\rangle_o - |11\text{-}10\rangle_c|1110\rangle_o \right\}$$

$$^3\Sigma^+_{-1} = \frac{1}{\sqrt{2}} \left\{ |1100\rangle_c |11\text{-}10\rangle_0 - |11\text{-}10\rangle_c |1100\rangle_0 \right\}$$

$$^5\Sigma^+_{+2} = |1110\rangle_c |1110\rangle_0$$

$$^5\Sigma^+_{+1} = \frac{1}{\sqrt{2}} \left\{ |1110\rangle_c |1100\rangle_0 + |1100\rangle_c |1110\rangle_0 \right\}$$

$$^5\Sigma^+_0 = \frac{1}{\sqrt{6}} \left\{ |1110\rangle_c |11\text{-}10\rangle_0 + 2|1100\rangle_c |1100\rangle_0 + |11\text{-}10\rangle_c |1110\rangle_0 \right\}$$

$$^5\Sigma^+_{-1} = \frac{1}{\sqrt{2}} \left\{ |1100\rangle_c |11\text{-}10\rangle_0 + |11\text{-}10\rangle_c |1100\rangle_0 \right\}$$

$$^5\Sigma^+_{-2} = |11\text{-}10\rangle_c |11\text{-}10\rangle_0$$

$$^1\Pi_0 = \pm \frac{1}{\sqrt{3}} \left\{ |111\pm1\rangle_c |11\text{-}1\mp1\rangle_0 - |11\text{-}1\mp1\rangle_c |111\pm1\rangle_0 \right\}$$

$$^3\Pi_{\pm1} = \pm \frac{1}{\sqrt{2}} \left\{ |111\pm1\rangle_c |1100\rangle_0 - |1100\rangle_c |111\pm1\rangle_0 \right\}$$

$$^3\Pi_0 = \pm \frac{1}{\sqrt{2}} \left\{ |111\pm1\rangle_c |11\text{-}1\mp1\rangle_0 \right\}$$

$$^3\Pi_{-1} = \pm \frac{1}{\sqrt{2}} \left\{ |1110\rangle_c |11\text{-}1\mp1\rangle_0 \right\}$$

$$^5\Pi_{\pm2} = \pm |111\pm1\rangle_c |1110\rangle_0$$

$$^5\Pi_{\pm1} = \pm \frac{1}{\sqrt{2}} \left\{ |111\pm1\rangle_c |1100\rangle_0 + |1100\rangle_c |111\pm1\rangle_0 \right\}$$

$$^5\Pi_0 = \pm \frac{1}{\sqrt{6}} \left\{ |111\pm1\rangle_c |11\text{-}1\mp1\rangle_0 + 2|1100\rangle_c |11\text{-}1\mp1\rangle_0 + |11\text{-}1\mp1\rangle_c |111\pm1\rangle_0 \right\}$$

$$^5\Pi_{-1} = \pm \frac{1}{\sqrt{2}} \left\{ |11\text{-}1\mp1\rangle_c |11\text{-}10\rangle_0 \right\}$$

$$^5\Pi_{-2} = \pm |111\pm1\rangle_c |11\text{-}10\rangle_0$$

$$^1\Pi_0 = \pm \frac{1}{\sqrt{3}} \left\{ |1110\rangle_c |11\text{-}1\mp1\rangle_0 - |11\text{-}10\rangle_c |111\pm1\rangle_0 + |111\pm1\rangle_c |11\text{-}1\mp1\rangle_0 \right\}$$

$$^3\Pi_{+1} = \pm\frac{1}{\sqrt{2}}\left\{|1110\rangle_c|110\pm1\rangle_o - |1100\rangle_c|111\pm1\rangle_o\right\}$$

$$^3\Pi_0 = \pm\frac{1}{\sqrt{2}}\left\{|1110\rangle_c|11-1\pm1\rangle_o - |11-10\rangle_c|111\pm1\rangle_o\right\}$$

$$^3\Pi_1 = \pm\frac{1}{\sqrt{2}}\left\{|1100\rangle_c|11-1\pm1\rangle_o - |11-10\rangle_c|110\pm1\rangle_o\right\}$$

$$^5\Pi_{+2} = \pm|1110\rangle_c|111\pm1\rangle_o$$

$$^5\Pi_{+1} = \pm\frac{1}{\sqrt{2}}\left\{|1110\rangle_c|110\pm1\rangle_o + |1100\rangle_c|111\pm1\rangle_o\right\}$$

$$^5\Pi_0 = \pm\frac{1}{\sqrt{6}}\left\{|1110\rangle_c|11-1\pm1\rangle_o + 2|1100\rangle_c|110\pm1\rangle_o + |11-10\rangle_c|111\pm1\rangle_o\right\}$$

$$^5\Pi_1 = \pm\frac{1}{\sqrt{2}}\left\{|1100\rangle_c|11-1\pm1\rangle_o + |11-10\rangle_c|110\pm1\rangle_o\right\}$$

$$^5\Pi_2 = \pm|11-10\rangle_c|11-1\pm1\rangle_o$$

$$^1\Delta_0 = \frac{1}{\sqrt{3}}\left\{|111\pm1\rangle_c|11-1\pm1\rangle_o - |110\pm1\rangle_c|110\pm1\rangle_o + |11-1\pm1\rangle_c|111\pm1\rangle_o\right\}$$

$$^3\Delta_{+1} = \frac{1}{\sqrt{2}}\left\{|111\pm1\rangle_c|110\pm1\rangle_o - |110\pm1\rangle_c|111\pm1\rangle_o\right\}$$

$$^3\Delta_0 = \frac{1}{\sqrt{2}}\left\{|111\pm1\rangle_c|11-1\pm1\rangle_o - |11-1\pm1\rangle_c|111\pm1\rangle_o\right\}$$

$$^3\Delta_{-1} = \frac{1}{\sqrt{2}}\left\{|110\pm1\rangle_c|11-1\pm1\rangle_o - |11-1\pm1\rangle_c|110\pm1\rangle_o\right\}$$

$$^5\Delta_{+2} = |111\pm1\rangle_c|111\pm1\rangle_o$$

$$^5\Delta_{+1} = \frac{1}{\sqrt{2}}\left\{|111\pm1\rangle_c|110\pm1\rangle_o + |110\pm1\rangle_c|111\pm1\rangle_o\right\}$$

$$^5\Delta_0 = \frac{1}{\sqrt{6}}\left\{|111\pm1\rangle_c|11-1\pm1\rangle_o + 2|110\pm1\rangle_c|110\pm1\rangle_o + |11-1\pm1\rangle_c|111\pm1\rangle_o\right\}$$

$$^5\Delta_{-1} = \frac{1}{\sqrt{2}}\left\{|110\pm1\rangle_c|11-1\pm1\rangle_o + |11-1\pm1\rangle_c|110\pm1\rangle_o\right\}$$

$$^5\Delta_{-2} = |11-1\pm1\rangle_c|11-1\pm1\rangle_o$$

18 Molecular states:

$6\Sigma^+ 2\pi(^{1,3,5}\Sigma^+)$

$6\Pi 2\pi(^{1,3,5}\Pi)$

$3\Sigma^- (^{1,3,5}\Sigma^-)$

$3\Delta (^{1,3,5}\Delta)$

Appendix II: Molecular basis functions for C(^3P_J) + O(^3P_J) interaction

1. $^3P_0$(C) + $^3P_2$(O) interaction: E_{diss} = 0.0 cm⁻¹   **3 states**

$$0^+ = |00\rangle_C |20\rangle_O$$
$$1 = \pm|00\rangle_C |2\pm1\rangle_O$$
$$2 = |00\rangle_C |2\pm2\rangle_O$$

2. $^3P_1$(C) + $^3P_2$(O) interaction: E_{diss} = 16.4 cm⁻¹   **9 states**

$$0^+ = \frac{1}{\sqrt{2}}\{|1\,{-}1\rangle_C|21\rangle_O - |11\rangle_C|2\,{-}1\rangle_O\}$$
$$0^- = \frac{1}{\sqrt{2}}\{|1\,{-}1\rangle_C|21\rangle_O + |11\rangle_C|2\,{-}1\rangle_O\}$$
$$0^- = |10\rangle_C|20\rangle_O$$
$$1 = |1\pm1\rangle_C|20\rangle_O$$
$$1 = |10\rangle_C|2\pm1\rangle_O$$
$$1 = |1\mp1\rangle_C|2\pm2\rangle_O$$
$$2 = \pm|1\pm1\rangle_C|2\pm1\rangle_O$$
$$2 = \pm|10\rangle_C|2\pm2\rangle_O$$
$$3 = |1\pm1\rangle_C|2\pm2\rangle_O$$

3. $^3P_2$(C) + $^3P_2$(O) interaction: E_{diss} = 43.4 cm⁻¹   **14 states**

$$0^+ = \frac{1}{\sqrt{2}}\{|2\,{-}2\rangle_C|2\,2\rangle_O + |22\rangle_C|2\,{-}2\rangle_O\}$$
$$0^+ = \frac{1}{\sqrt{2}}\{|2\,{-}1\rangle_C|2\,1\rangle_O + |21\rangle_C|2\,{-}1\rangle_O\}$$
$$0^- = \frac{1}{\sqrt{2}}\{|2\,{-}2\rangle_C|2\,2\rangle_O - |22\rangle_C|2\,{-}2\rangle_O\}$$
$$0^- = \frac{1}{\sqrt{2}}\{|2\,{-}1\rangle_C|2\,1\rangle_O - |2\,1\rangle_C|2\,{-}1\rangle_O\}$$
$$0^+ = |2\,0\rangle_C|2\,0\rangle_O$$
$$1 = \pm|2\pm1\rangle_C|2\,0\rangle_O$$
$$1 = \pm|20\rangle_C|2\pm1\rangle_O$$
$$1 = \pm|2\mp1\rangle_C|2\pm2\rangle_O$$

$2 = |2 \pm 2\rangle_C |2\ 0\rangle_O$

$2 = |2 \pm 1\rangle_C |2 \pm 1\rangle_O$

$2 = |2\ 0\rangle_C |2 \pm 2\rangle_O$

$3 = \pm |2 \pm 2\rangle_C |2 \pm 1\rangle_O$

$3 = \pm |2 \pm 1\rangle_C |2 \pm 2\rangle_O$

$4 = |2 \pm 2\rangle_C |2 \pm 2\rangle_O$

4. $^3P_0(C) + {}^3P_1(O)$ interaction: $E_{diss} = 158.3$ cm^{-1} 2 states

$0^- = |0\ 0\rangle_C |1\ 0\rangle_O$

$1 = |0\ 0\rangle_C |1 \pm 1\rangle_O$

5. $^3P_1(C) + {}^3P_1(O) = E_{diss}$ interaction: 174.7 cm^{-1} 6 states

$0^+ = \frac{1}{\sqrt{2}} \{ |1 - 1\rangle_C |1\ 1\rangle_O + |1\ 1\rangle_C |1 - 1\rangle_O \}$

$0^+ = |1\ 0\rangle_C |1\ 0\rangle_O$

$0^- = \frac{1}{\sqrt{2}} \{ |1 - 1\rangle_C |1\ 1\rangle_O - |1\ 1\rangle_C |1 - 1\rangle_O \}$

$1 = \pm |1 \pm 1\rangle_C |1\ 0\rangle_O$

$1 = \pm |1\ 0\rangle_C |1 \pm 1\rangle_O$

$2 = |1 \pm 1\rangle_C |1 \pm 1\rangle_O$

6. $^3P_2(C) + {}^3P_1(O)$ interaction: $E_{diss} = 201.7$ 9 states

$$0^+ = \frac{1}{\sqrt{2}} \{ |2\ 1\rangle_C |1 - 1\rangle_O - |2 - 1\rangle_C |1\ 1\rangle_O \}$$

$$0^- = \frac{1}{\sqrt{2}} \{ |2\ 1\rangle_C |1 - 1\rangle_O + |2 - 1\rangle_C |1\ 1\rangle_O \}$$

$$0^- = |2\ 0\rangle_C |1\ 0\rangle_O$$

$$1 = |2\ 0\rangle_C |1 \pm 1\rangle_O$$

$$1 = |2 \pm 1\rangle_C |1\ 0\rangle_O$$

$$1 = |2 \pm 2\rangle_C |1 \overline{+} 1\rangle_O$$

$$2 = \pm |2 \pm 1\rangle_C |1 \pm 1\rangle_O$$

$$2 = \pm |2 \pm 2\rangle_C |1\ 0\rangle_O$$

$$3 = |2 \pm 2\rangle_C |1 \pm 1\rangle_O$$

7. $^3P_0(C) + {}^3P_0(O)$ interaction $= E_{diss} = 227$ cm^{-1} 1 state

$$0^+ = |0\ 0\rangle_C |0\ 0\rangle_O$$

8. $^3P_1(C) + {}^3P_0(O)$ interaction $\approx E_{diss} = 243.4$ cm^{-1} 2 states

$$0^- = |1\ 0\rangle_O |0\ 0\rangle_O$$

$$1 = |1 \pm 1\rangle_C |0\ 0\rangle_O$$

9. $^3P_2(C) + {}^3P_0(O)$ interactions $= E_{diss} \doteq 270.4$ cm^{-1} 3 states

$$0^+ = |2\ 0\rangle_C |0\ 0\rangle_O$$

$$1 = \pm |2 \pm 1\rangle_C |0\ 0\rangle_O$$

$$2 = |2 \pm 2\rangle_C |0\ 0\rangle_O$$

Total: 43 molecular states

Appendix III: 2p Orbital SCF Wavefunctions for Carbon and Oxygen Atoms

$$\Psi_{(2p)} = \sum_i N_i \, C_i \, r^{N_i - 1} \, e^{-\zeta_i} \, Y_i^{m_i} (\theta, \Phi)$$

Atom	n	l	ζ_i	$C_i\,(2p\sigma)$	$C_i\,(2p\sigma)$
C	2	1	6.51	-.010247216	-.0102472161
	2	1	2.6005	-.2319540338	-.2319540339
	2	1	1.4436	-.5469976538	-.5469976544
	2	1	.9807	-.2823784197	-.2823784190
O	2	1	7.5648	-.0765520772	-.0165527165
	2	1	3.4499	-.3277071772	-.3225525816
	2	1	1.8173	-.6188261938	-.5656618839
	2	1	1.1439	-.1184586922	-.1867904703

2s Orbital HF Wavefunctions for Carbon and Oxygen Atoms

Atom	n	l	ζ_i	C_i
C	1	0	9.4826	.0107111691
	1	0	5.4360	.2081422862
	2	0	4.2010	.1476498490
	2	0	2.6844	-.3354681690
	2	0	1.5243	-.7504500909
	2	0	1.0575	-.0810066997
O	1	0	13.7574	-.0047624085
	1	0	7.6141	-.2215772275
	2	0	5.8660	-.1918271486
	2	0	4.3120	.2536208043
	2	0	2.4802	.6082459022
	2	0	1.6982	.3482806491

Appendix IV: Explicit E_5 and E_6 Matrix Elements for $^{1,3,5}\Sigma^+$, $^{1,3,5}\Sigma^-$, and $^{1,3,5}\Delta$ molecular states in terms of $\mathfrak{R}^2_{ab}$ and $\mathfrak{R}_{\alpha\beta}$ with $\alpha, \beta \in \{0,1,2\}$ $\mathfrak{R}^2_{ab}$ and $\mathfrak{R}_{\alpha\beta} = \mathfrak{R}^{1111}_{\alpha\beta}$ are given by the relations (1) and (2) respectively.

1. $^{1,3,5}\Sigma^+$ states

$$\begin{bmatrix} E_5(1,1) & E_5(1,2) \\ & E_5(2,2) \end{bmatrix} = \begin{bmatrix} \frac{4}{10} & .5656854 \\ & \frac{8}{10} \end{bmatrix} \mathfrak{R}^2_a \mathfrak{R}^2_b$$

$$\begin{bmatrix} E_6(1,1) & E_6(1,2) \\ & E_6(2,2) \end{bmatrix} = \begin{bmatrix} \frac{2}{9} & .31426968 \\ & \frac{4}{9} \end{bmatrix} \mathfrak{R}_{00} + \begin{bmatrix} \frac{2}{90} & -.0628539 \\ & \frac{8}{45} \end{bmatrix} (\mathfrak{R}_{02} + \mathfrak{R}_{20})$$

$$+ \begin{bmatrix} \frac{5}{30} & .0785674 \\ & \frac{5}{90} \end{bmatrix} \mathfrak{R}_{11} + \begin{bmatrix} -\frac{2}{30} & .04714045 \\ & -\frac{1}{30} \end{bmatrix} (\mathfrak{R}_{12} + \mathfrak{R}_{21}) + \begin{bmatrix} \frac{37}{450} & .040855 \\ & \frac{41}{450} \end{bmatrix} \mathfrak{R}_{22}$$

2. $^{1,3,5}\Sigma^-$ states:

$$E_5(1,1) = C_5(1) = O$$
$$E_6(1,1) = C_5(1) = -\frac{1}{9}(\mathfrak{R}_{01} + \mathfrak{R}_{10}) + \frac{1}{9}\mathfrak{R}_{11} - \frac{7}{90}(\mathfrak{R}_{12} + \mathfrak{R}_{21}) + \frac{8}{100}\mathfrak{R}_{22}$$

3. $^{1,3,5}\Pi$ states:

$$\begin{bmatrix} E_5(1,1) & E_5(1,2) \\ & E_5(2,2) \end{bmatrix} = \begin{bmatrix} -\frac{4}{10} & -\frac{4}{10} \\ & -\frac{4}{10} \end{bmatrix} \mathfrak{R}^2_a \mathfrak{R}^2_b$$

$$\begin{bmatrix} E_6(1,1) & E_6(1,2) \\ & E_6(2,2) \end{bmatrix} = \begin{bmatrix} -\frac{5}{90} & -\frac{1}{9} \\ & \frac{2}{9} \end{bmatrix} \mathfrak{R}_{01} + \begin{bmatrix} \frac{1}{30} & -\frac{2}{30} \\ & \frac{4}{30} \end{bmatrix} \mathfrak{R}_{02} + \begin{bmatrix} -\frac{2}{9} & -\frac{1}{9} \\ & \frac{5}{90} \end{bmatrix} \mathfrak{R}_{10}$$

$$+ \begin{bmatrix} \frac{25}{900} & 0 \\ & \frac{25}{900} \end{bmatrix} \mathfrak{R}_{11} + \begin{bmatrix} -\frac{95}{900} & +\frac{2}{90} \\ & -\frac{35}{900} \end{bmatrix} \mathfrak{R}_{12} + \begin{bmatrix} \frac{4}{30} & -\frac{2}{30} \\ & \frac{1}{30} \end{bmatrix} \mathfrak{R}_{20} + \begin{bmatrix} -\frac{35}{900} & +\frac{2}{9} \\ & -\frac{95}{900} \end{bmatrix} \mathfrak{R}_{21} + \begin{bmatrix} \frac{23}{300} & 3 \\ & 3 \end{bmatrix}$$

4. $^{1,3,5}\Delta$ states:

$$E_5(1,1) = C_5(1) = \frac{2}{10}\mathfrak{R}^2_a \mathfrak{R}^2_b$$

$$E_6(1,1) = C_6(1) = \frac{2}{30}(\mathfrak{R}_{02} + \mathfrak{R}_{20}) + \frac{1}{9}\mathfrak{R}_{11} - \frac{1}{10}(\mathfrak{R}_{12} + \mathfrak{R}_{21}) + \frac{16}{300}\mathfrak{R}_{22}$$